Fermi National Accelerator Laboratory

Radiation Effects in Intrinsic 3HF Scintillator

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ABSTRACT

Test scintillators of the type 3-hydroxyflavone (3HF) plus polystyrene were prepared with 3HF doping concentrations between 0.05% and 2.0% by weight. Ternary scintillators of the type p-terphenyl(1%) + 3HF(0.01%) and p-terphenyl(1%) + 3HF(0.1%) in polystyrene were also prepared. The scintillation light yield is given for all samples. Representative fluorescence and transmittance spectra are also shown. Changes in light yield, transmittance, and fluorescence are shown for ^{60}Co irradiations with integrated doses of 10 and 30 Mrad.

I. Introduction

Renewed interest in plastic scintillator has been largely driven by the development of high-quality plastic scintillating optical fiber (PSF). In recent years, numerous detectors[1-7] have been constructed using PSF, and many have already been operated successfully in experiments. This study was motivated by the detector challenges that will exist at future accelerators such as the Super Conducting Supercollider (SSC) or the Large Hadron Collider (LHC). Tracking systems and calorimetry will have to operate at very high luminosity and must be able to tolerate radiation exposures of up to tens of megarads. Many groups[8-14] have addressed the need to develop new scintillators that can operate in this type of environment.

In order to minimize the effects of radiation-induced polymer degradation, we have been developing intrinsic[15] plastic scintillators. "Intrinsic" in this sense means that only one dopant is added to the polymer base (polystyrene in this case). When ionizing radiation deposits energy in the polymer, some of this excitation energy is transferred from the polymer molecules to the dopant via the Förster[16] mechanism. The dopant can then return to its ground state with the emission of a photon (scintillation fluorescence). Radiation-induced color centers in the polymer do not influence this mechanism very strongly, since Förster transfer occurs on a distance scale of angstroms. However, if a plastic scintillator is designed with more than one dopant, i.e., using a primary and a secondary (wavelength shifting) dye, the new absorption in the polymer, often referred to as radiation-induced hidden absorption[17], can have a measurable effect on the transfer efficiency between the primary and the secondary dopant. (The term "hidden" is used to reflect that, in this type of scintillator, the absorption of the dopants masks most of the radiation-induced absorption in the polymer.) This effect is particularly true for primaries such as p-terphenyl that emit in the near UV. Since intrinsic plastic scintillators eliminate the need for a secondary dopant they can, in principle, be less susceptible to radiation effects if the dopant's fluorescence is not affected by radiation-induced transmission losses. Scintillators that incorporate 3-hydroxyflavone (3HF) have

been shown to exhibit good radiation stability. Nevertheless, those that use 3HF as a secondary can still exhibit light loss due to radiation-induced hidden absorption in the polymer competing with energy transfer from the primary to the secondary (3HF). But, since 3HF will couple directly to polystyrene excitation, it can also be used as a primary in an intrinsic plastic scintillator. In addition, 3HF exhibits a very large Stokes shift between its absorption maximum (350 nm) and its emission peak (530 nm) and thus shifts the scintillator's fluorescence to a spectral region where transmission losses are small, even after irradiation. In this way, absorption effects, over relatively long distances, can be minimized. Another advantage of intrinsic plastic scintillator is in applications that require very small diameter (on the order of a few hundred microns) fibers. Since the mean-free-path (mfp) for up-conversion for a typical ternary plastic scintillator is approximately 100 to 200 microns, fiber of diameter on the order of this mfp will suffer from light loss due to the primary fluorescence leaving the fiber before up-conversion. This problem is eliminated in intrinsic scintillator.

II. Sample Preparation

Styrene monomer was first deinhibited using column chromatography and then was purified by vacuum distillation. Glass polymerization tubes were cleaned with nitric and sulfuric acids, rinsed with distilled water, and then treated for about 4 h with a 30% solution of dichlorodimethylsilane in chloroform. Finally, they were rinsed in turn with chloroform, methanol, and distilled water. This treatment builds a hydrophobic Langmuir layer on the walls of the tube which enables the removal of the plastic after polymerization. 3HF was purchased from Aldrich Chemical Co. and was purified through recrystallization from methylene chloride/hexane solutions. p-Terphenyl was purchased from Bicron Corporation and was used in the two ternary scintillators without additional purification. The appropriate dopant(s) was(were) then added to the purified styrene, and the solutions were then placed in the polymerization tubes and degassed with repeated freeze-pump-thaw cycles. Polymerization was carried out in a silicone oil bath at 90 °C

for 2 h, at 110 °C for 24 h, at 125 °C for 48 h, and finally at 140 °C for 12 h. After this cycle, the bath was ramped down to 90 °C at a rate of 10 °C/h. After removal from the oil bath, the tubes were quenched in liquid nitrogen for a fast release of the plastic rods. The rods were then cut and polished into either discs of 2.2 cm diameter and 1 cm thick or rods of 2.2 cm diameter and 10 cm long.

III. Instrumentation and Techniques

The scintillator samples were prepared with 3HF concentrations (wt. percent) between .05% and 2.0%. In addition, two ternary scintillators using p-terphenyl plus 3HF were also prepared (1% p-terphenyl + 0.01% 3HF and 1% p-terphenyl + 0.1% 3HF). Transmittance and fluorescence spectra were measured with a Hewlett-Packard model 8451A diode array spectrophotometer. All transmittance measurements used pure (undoped) polystyrene as the reference. The fluorescence spectra were measured using an external Hg lamp whose light was brought into the spectrophotometer by means of a quartz fiber. An excitation wavelength of 313 nm was selected with the use of a bandpass filter. Front-surface (FS) excitation measurements were recorded in which the quartz fiber was positioned to excite the sample surface closest to the detector with the excitation light impinging at an angle of incidence of 45°, Figure 1. These measurements were done in order to monitor any radiation-induced degradation of the dopants independent of any polymer effects. Any significant decrease in the fluorescence area after irradiation might indicate that the dopant is degraded under irradiation. Only transmittance measurements were performed on the 10 cm long samples.

III.1. LIGHT YIELD MEASUREMENTS

Scintillation light yield measurements used 1 MeV conversion electrons from [207]Bi as the excitation source. A Hamamatsu R669 photomultiplier (PMT) was used as the detector. Over the wavelength range of 3HF fluorescence, this tube has a quantum yield of between 18% and 20%. The 1 cm scintillator samples were

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placed directly on the photomultiplier using mineral oil for optical contact, and the pulse height spectra were recorded with a LeCroy qVt multi-channel analyzer. The 10 cm long samples were not used for light yield determination, since we wished to separate the effect of transmission loss from changes in scintillation or "technical" light yield. Technical light yield is the yield from small sample scintillators where the effects of self absorption are minimized. A typical spectrum for one of the samples is shown in Figure 2. The two main features of this spectrum are the 1 MeV electron peak and the compton edge from 1 MeV photon conversions. The overall reproducibility of these measurements is dominated by sample surface preparation and condition and is approximately ± 2.0%.

III.2. RADIATION EXPOSURES

The samples for radiation damage studies were placed in stainless steel cans and then evacuated for a week to remove all moisture and most gas from the samples. The cans were then back-filled with dry nitrogen. All samples were irradiated with a ^{60}Co source at the Nuclear Reactor Laboratory of the University of Michigan, at a rate of 1 Mrad/h. The 1 cm intrinsic 3HF scintillator samples were first exposed to a total dose of 10 Mrad. Measurements were performed on these samples immediately after this irradiation, and the samples were then fully annealed (see below). A second irradiation then exposed the same samples to an additional dose of 20 Mrad for a total exposed sample dose of 30 Mrad. The 10 cm samples and the ternary 3HF scintillators were given a single 10 Mrad exposure. During the irradiations, the sample temperature was held constant to approximately 5 °C. Immediately after irradiation, all the samples showed some coloration which partially disappeared with time. This "annealing" phenomenon is due to the relaxation of excited species that were created during the irradiation. The annealing period for samples of this size (2.2 cm diameter) is approximately 25 days in air and at room temperature. However, this process can be greatly accelerated (Reference 13) if the samples are placed in a pressurized oxygen atmosphere (40 psig.). Under the latter conditions, the samples are annealed in about 7 days. For this study, the

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samples were annealed in an oxygen atmosphere (40 psig.) for 10 days, were then removed and measured, and then were left in air until subsequent measurements showed no additional annealing. We have seen changes of up to +10% in transmittance (in the deep blue spectral region) occurring during a relatively long (1-2 month) anneal in air, even after the sample had been annealed in oxygen.

IV. Results

Figure 3 gives data for the initial (before irradiation) light yield of the 1 cm 3HF scintillator samples as a function of 3HF doping concentration. As can be seen from this figure, maximum light yield occurs at a concentration of 1 percent which is similar to the concentration used for primaries in the more standard ternary plastic scintillators. As a reference, the yield for BC 408 and for the ternary scintillators using p-terphenyl as the primary (1%) and 3HF as the secondary (0.01% and 0.10%) are also shown. Figure 4 shows how the absorption edge shifts to longer wavelengths as the 3HF concentration is increased. The fluorescence distribution for 3HF is also given in this figure.

As described above, the 1 cm intrinsic 3HF scintillator samples were irradiated to 10 Mrad, measured, fully annealed, remeasured, irradiated with an additional 20 Mrad, measured, fully annealed for a second time, and finally measured again after this second anneal. Each annealing period corresponded to a high pressure oxygen anneal plus a long-term (2 month) air anneal. Multiple measurements were taken during the air anneal. Figure 5 shows the pulse height data for the 1% 3HF sample before irradiation and immediately after the 10 Mrad exposure. Figure 6 shows, as a function of 3HF concentration, the ratio of the light yield measured immediately after the 10 and 20 (30 total) Mrad exposures to the initial (before any irradiation) light yield for the samples. Figure 7 shows the same data, but, in each case, is after the full anneal. We also show data for the two ternary 3HF scintillators on this plot. From these last two Figures, we see that the annealing is quite significant, the 1% sample recovers to 97% of its initial light yield. However, even after the anneal,

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the light yield loss for the low concentration intrinsic samples is significant, 17% for the 0.05% sample and 12% for the 0.10% sample. For the ternary scintillator with 0.01% 3HF, the light yield loss after a 10 Mrad dose and after annealing was also approximately 17%. However, the sample with 1% p-terphenyl + 0.10% 3HF had only a 6% loss in yield.

Figures 8 - 12 give transmittance data for five of the samples for five different conditions: before irradiation, immediately after the 10 Mrad dose, after the first annealing period, immediately after the 20 Mrad dose, and after the final anneal. As can be seen from these figures, the radiation-induced absorption is stronger at shorter wavelengths and is also more pronounced the higher the 3HF concentration. At low concentration, the observed light yield loss cannot be explained by transmittance loss alone. At high concentration, the light yield loss can be attributed almost entirely to transmittance loss. These statements apply to measurements made both immediately after the irradiations and after the annealing processes. Figures 13 and 14 summarize the transmittance data for the 1 cm samples. They show the fractional transmittance loss, initial transmittance (T_o) - transmittance after irradiation (T_{ir}), as a function of 3HF concentration, for measurements done immediately after the two exposures and after the two anneal periods. The loss shown in these curves was measured at the wavelength of peak fluorescence for 3HF, $\lambda_{fl}^p = 530$ nm. Given that the changes after the 10 Mrad dose were small for the 1 cm samples, we used the 10 Mrad exposure of the 10 cm long samples to verify these measurements. Figures 15 - 17 give transmittance data for three 10 cm long samples. Transmittance loss data (after anneal) for the 10 cm samples are included in Figure 14 . As we can see from this Figure, the radiation-induced transmittance losses are small even for 10 cm sample path lengths. The instrumental uncertainty for transmittance measurements is approximately ± 0.5%.

At issue is whether or not the 3HF itself is significantly affected by the radiation. For samples with 3HF concentration greater than 0.25%, front surface UV-excitation measurements show little change in fluorescence after the irradiation. Figure 18 shows the fluorescence for the 1% sample both before and imme-

diately after the 10 Mrad exposure, and after the first anneal cycle. These data indicate that there is little change in the fluorescence However, for samples with low concentration there is a measurable effect. We have previously reported on this effect (Reference 17) in 3HF samples with 0.01% doping. Although a large decrease in the fluorescence yield from low concentration 3HF samples is observed when 313 nm light is used for excitation, the effect becomes significantly smaller when longer wavelength (380 nm) light is used. We believe that this indicates that the 3HF is not significantly affected by the radiation, but that radiation-induced polymer hidden absorption competes with 3HF absorption of the excitation light, particularly for samples that are doped with 3HF at low concentration, $\leq 0.1\%$.

In order to further investigate this issue, we prepared some special samples with 3HF crystals that had been irradiated (100 Mrad dose) prior to their incorporation in polystyrene scintillator samples. This 3HF was used to prepare a ternary scintillator, 1% p-terphenyl + 0.01% 3HF, following the procedure described above. Referenced to an identical sample made with non-irradiated 3HF crystals, we saw no difference in light yield and the spectral properties of the two samples were similar, Figure 19 .

One final analysis was performed on 3HF-doped scintillator samples in order to detect any radiation-induced degradation of the 3HF molecule. Three solutions were prepared by dissolving small amounts of non-irradiated 1% 3HF scintillator, irradiated (30 Mrad) 1% 3HF scintillator, and irradiated (30 Mrad) 0.75% 3HF scintillator in tetrahydrofuran (THF). These solutions were run through a High Performance Liquid Chromatograph (HPLC) equipped with Gel Permeation Chromatography (GPC) columns and a diode array detector. The detector was set to monitor the absorbance at $\lambda = 254$ nm. The instrument generated a plot, generally referred to as a chromatogram, of the absorbance at $\lambda = 254$ nm as a function of time. The chromatograms exhibit several peaks, each peak corresponding to a different component of the sample. The area under the peak is proportional to the amount of that component in the sample. The peak corresponding to 3HF was identified by its absorbance spectrum. Figures 20 and 21 show the chromatograms

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of the 1% 3HF sample before and after irradiation, respectively. Although the shape and size of the polymer peak change considerably after irradiation, no significant change in the 3HF peak area can be observed. The peak at t = 40 min. corresponds to the monomer, styrene, and decreases with irradiation since it further polymerizes. For the 0.75% 3HF scintillator sample, the peak area scaled proportionally to the amount of 3HF present in this sample. These results indicate that 3HF in the polymer does not significantly decompose under irradiation.

V. Conclusions

Measurements on intrinsic 3HF scintillator show that, even at integrated doses of 30 Mrad, this type of scintillator shows a relatively small amount of radiation damage. After a 10 Mrad dose, intrinsic 3HF scintillator with a 1% doping exhibits only a 3% loss in technical light yield. For high 3HF concentration ($\gtrsim$ 0.25% doping), light yield losses in this type of scintillator can be completely attributed to radiation-induced transmission losses. At low 3HF doping concentrations in both intrinsic 3HF scintillator and in ternary 3HF scintillator (1% p-terphenyl + (0.01-0.1)% 3HF), radiation-induced hidden absorption in the polymer base (polystyrene) is the principal cause of light yield loss. Since radiation-induced polymer absorption increases with decreasing wavelength, the ternary system does mitigate the effect of hidden absorption. The use of the primary, p-terphenyl, shifts the 3HF coupling wavelength to 350 nm (p-terphenyl $\rightarrow$ 3HF) from 320 nm in the case of the intrinsic scintillator (polystyrene $\rightarrow$ 3HF). (The wavelengths of peak fluorescence for polystyrene and p-terphenyl are 320 nm and 350 nm respectively.) The 0.10% intrinsic 3HF scintillator exhibited a 12% light yield loss after 10 Mrad compared to the ternary 3HF (0.10%) scintillator which showed only a 6% loss. Of course, with regard to light yield, the 0.10% intrinsic 3HF scintillator was far from the optimal concentration of approximately 1%. In applications where light collection requires a long path length through the scintillator, radiation-induced transmission loss is likely a bigger concern than intrinsic light yield loss and, in

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this case, a ternary scintillator using 1% p-terphenyl and 0.10% 3HF would appear to be the best 3HF scintillator candidate for high radiation level environments.

VI. Acknowledgements

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FIGURE CAPTIONS

1) Setup for fluorescence measurements using front surface excitation.

2) Typical pulse height spectrum for one of the samples.

3) 3HF scintillator light yield as a function of the 3HF concentration in the polymer. In addition, the relative yields for Bicron 408, pure polystyrene, pT + 0.01% 3HF, and pT + 0.1% 3HF scintillator are shown.

4) 3HF transmittance as a function of 3HF concentration in the polymer: (A) 0.1% 3HF, (B) 0.5% 3HF, (C) 1.0% 3HF, (D) 1.5% 3HF, (E) 2.0% 3HF. Inset: 3HF fluorescence in polystyrene.

5) Pulse height data for the 1% 3HF sample before irradiation, (a), and immediately after a 10 Mrad dose, (b). In each case the dotted line represents a gaussian fit to the 1 MeV electron peak.

6) Ratio of the light yield measured immediately after the 10 and 20 Mrad exposures to the initial scintillator light yield for the intrinsic 3HF samples.

7) Ratio of the yield measured after the 10 and 20 Mrad exposures and after annealing to the initial scintillator light yield for the intrinsic 3HF samples. In addition, the same ratio for the pT + 0.01% 3HF and pT + 0.1% 3HF scintillators is given.

8) Transmittance data for 1 cm long 0.10% 3HF sample irradiated to 10 and 20 (30 total) Mrad.

9) Transmittance data for 1 cm long 0.50% 3HF sample irradiated to 10 and 20 (30 total) Mrad.

10) Transmittance data for 1 cm long 1.00% 3HF sample irradiated to 10 and 20 (30 total) Mrad.

11) Transmittance data for 1 cm long 1.50% 3HF sample irradiated to 10 and 20 (30 total) Mrad.

12) Transmittance data for 1 cm long 2.00% 3HF sample irradiated to 10 and 20 (30 total) Mrad.

13) Fractional transmittance loss for the intrinsic 3HF samples as a function of 3HF concentration immediately after the exposures, measured at $\lambda = 530$ nm.

14) Fractional transmittance loss for the intrinsic 3HF samples as a function of 3HF concentration after annealing, measured at $\lambda = 530$ nm. Also included on the plot are the data for the 10 cm samples (10 Mrad).

15) Transmittance data for 10 cm long 0.10% 3HF sample: (A) before irradiation, (B) immediately after 10 Mrad irradiation, and (C) after the annealing period in oxygen.

16) Transmittance data for 10 cm long 0.50% 3HF sample: (A) before irradiation, (B) immediately after 10 Mrad irradiation, and (C) after the annealing period in oxygen.

17) Transmittance data for 10 cm long 1.00% 3HF sample: (A) before irradiation, (B) immediately after 10 Mrad irradiation, and (C) after the annealing period in oxygen.

18) Fluorescence data for the 1% 3HF sample.

19) Pulse height data from two samples of 1% p-terphenyl + 0.01% 3HF scintillator, (a) non-irradiated 3HF crystals, (b) irradiated (100 Mrad) 3HF crystals. In each case the dotted line represents a gaussian fit to the 1 MeV electron peak.

20) Chromatogram of a 1% 3HF/polystyrene sample in THF before irradiation.

21) Chromatogram of a 1% 3HF/polystyrene sample in THF after a 30 Mrad exposure.

Spectrophotometer input optics

Fluorescence

UV excitation

Sample
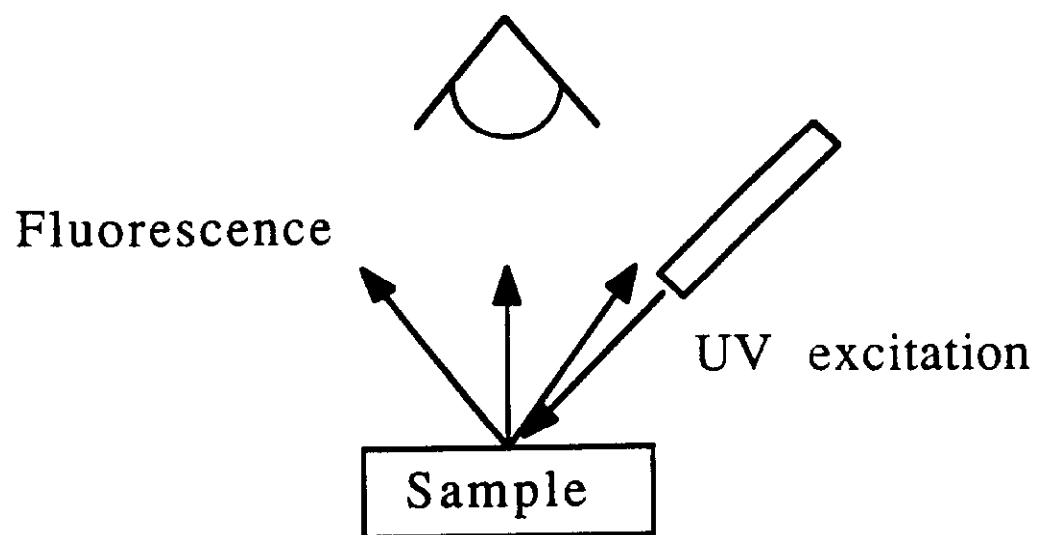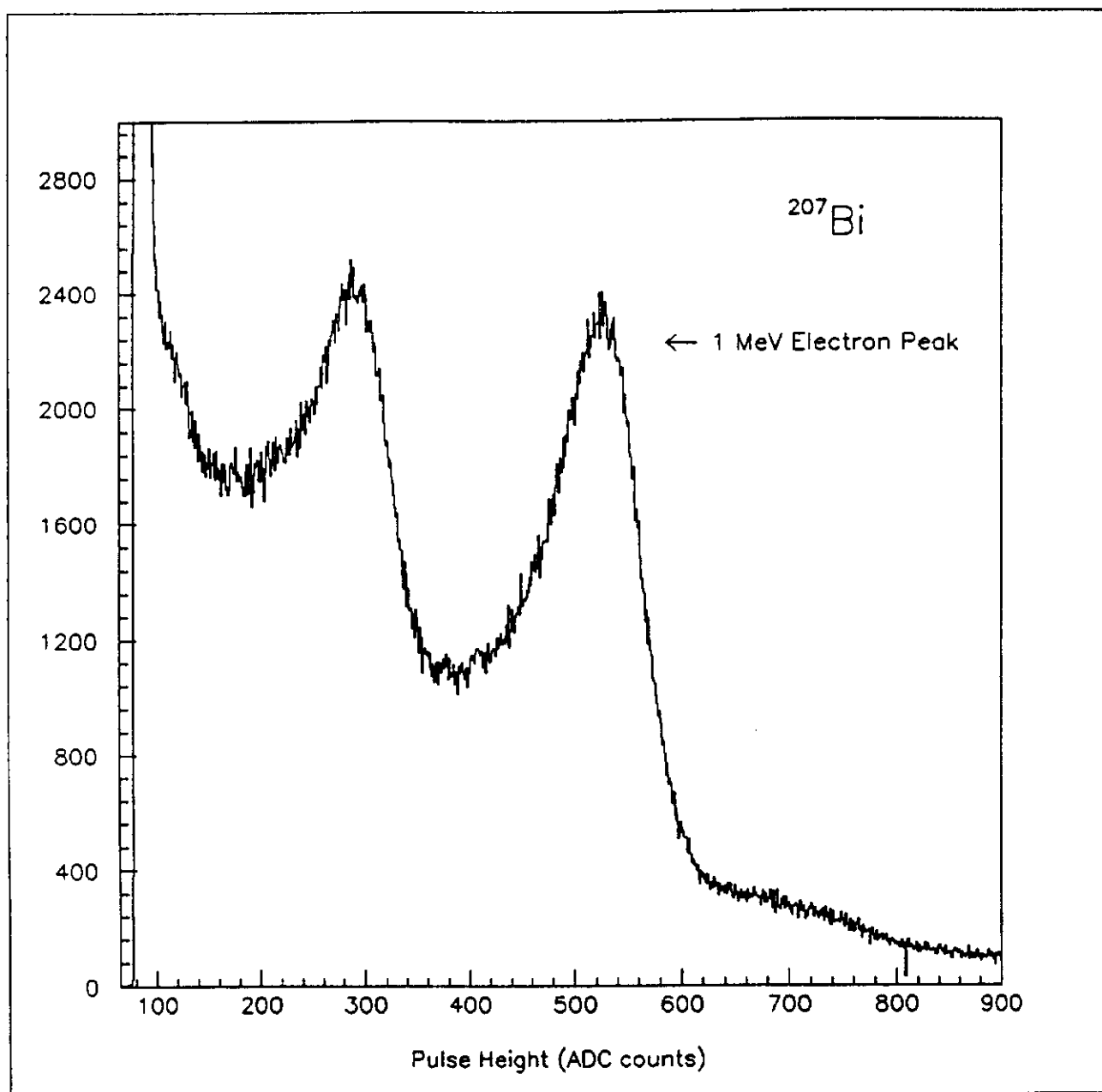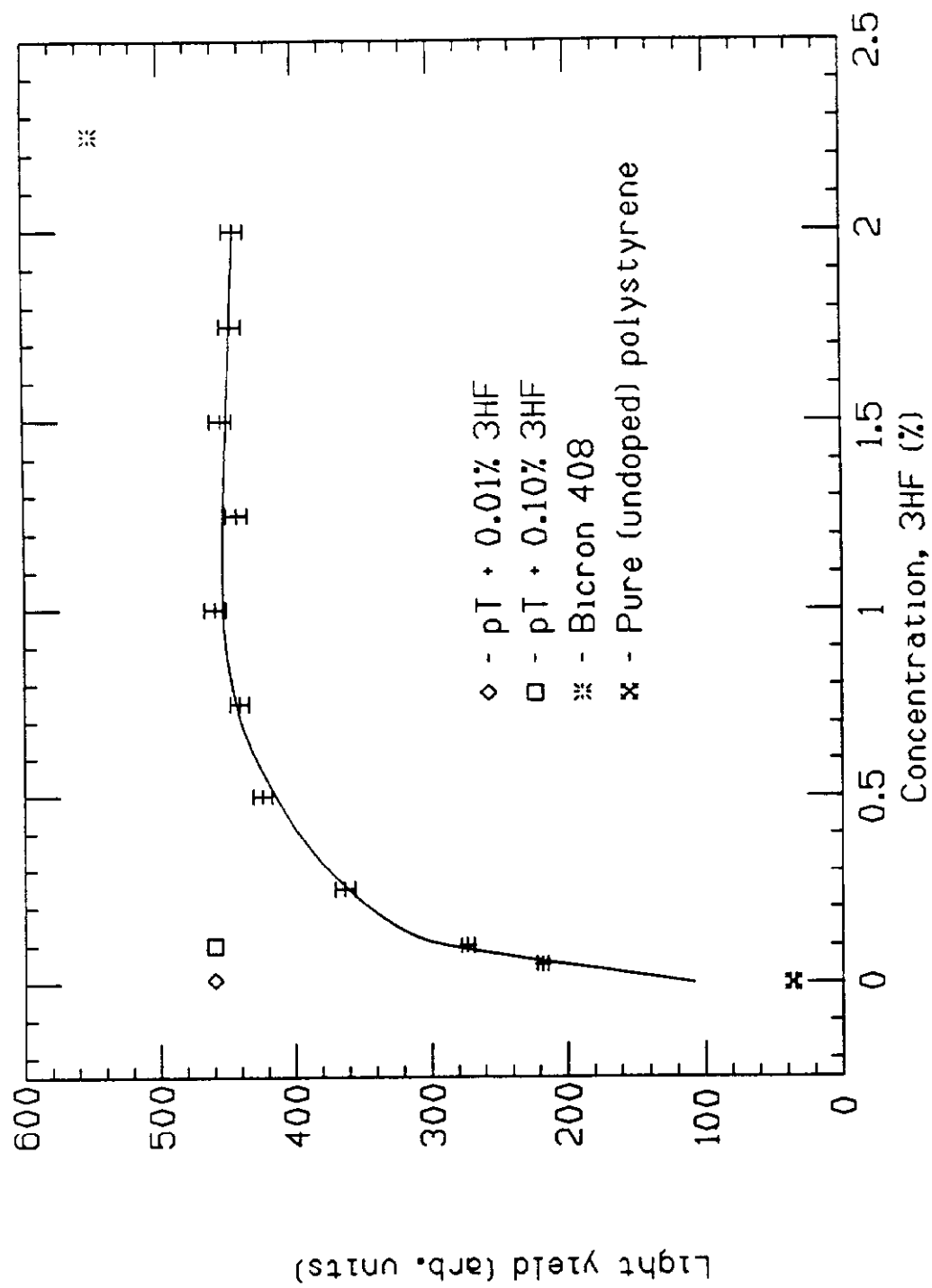
FIGURE 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5
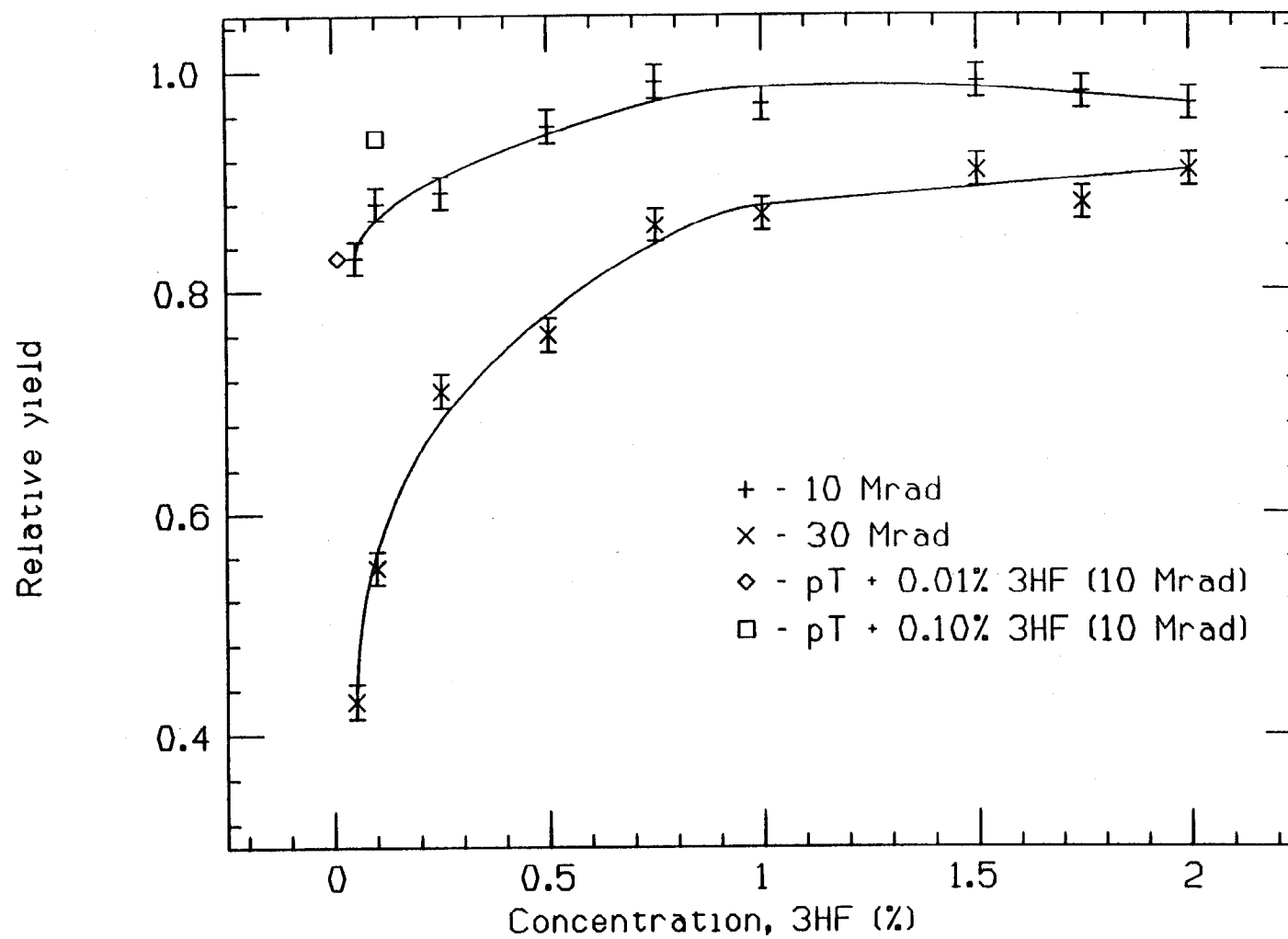
Relative yield

Concentration, 3HF (%)

+ - 10 Mrad
x - 30 Mrad
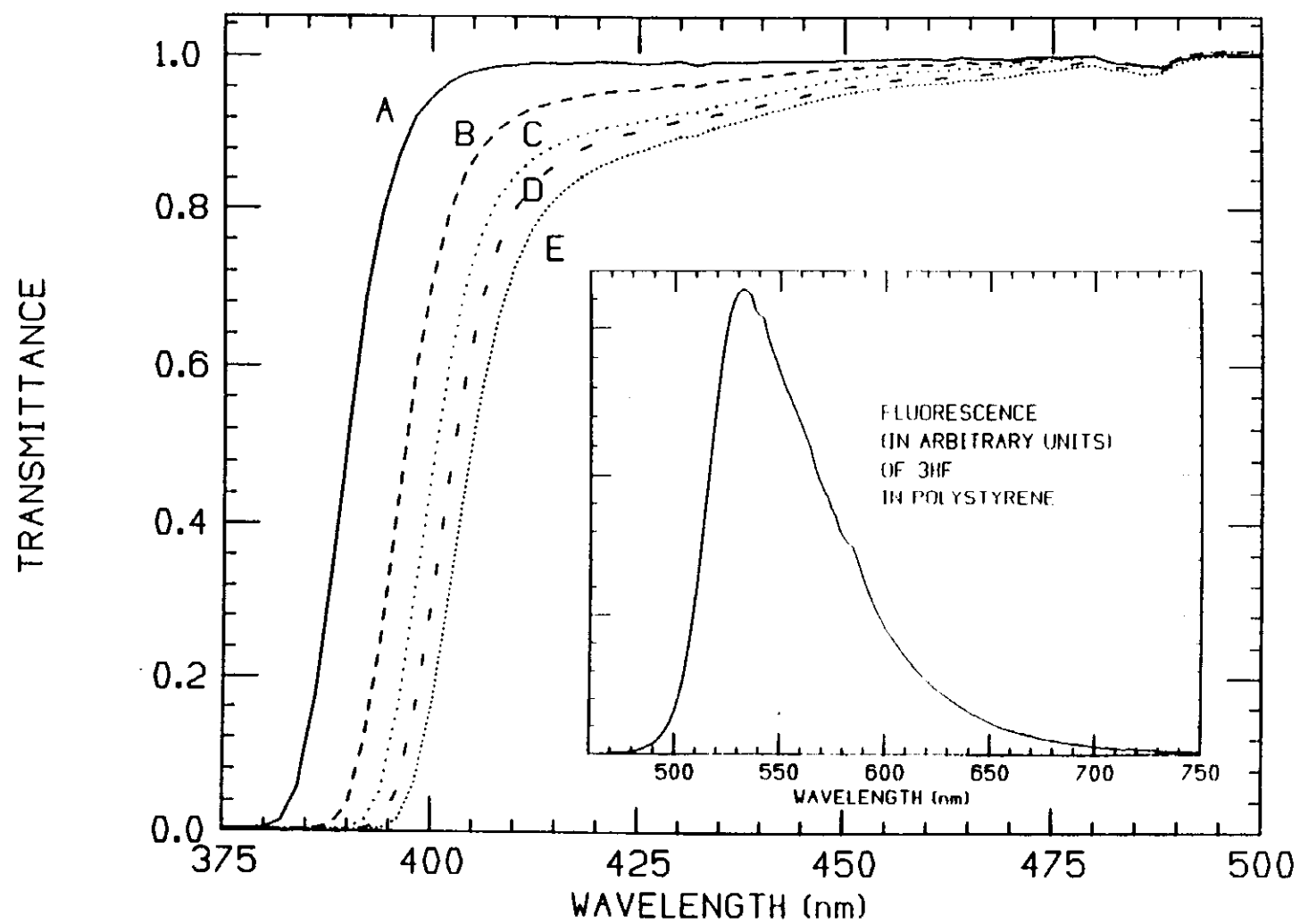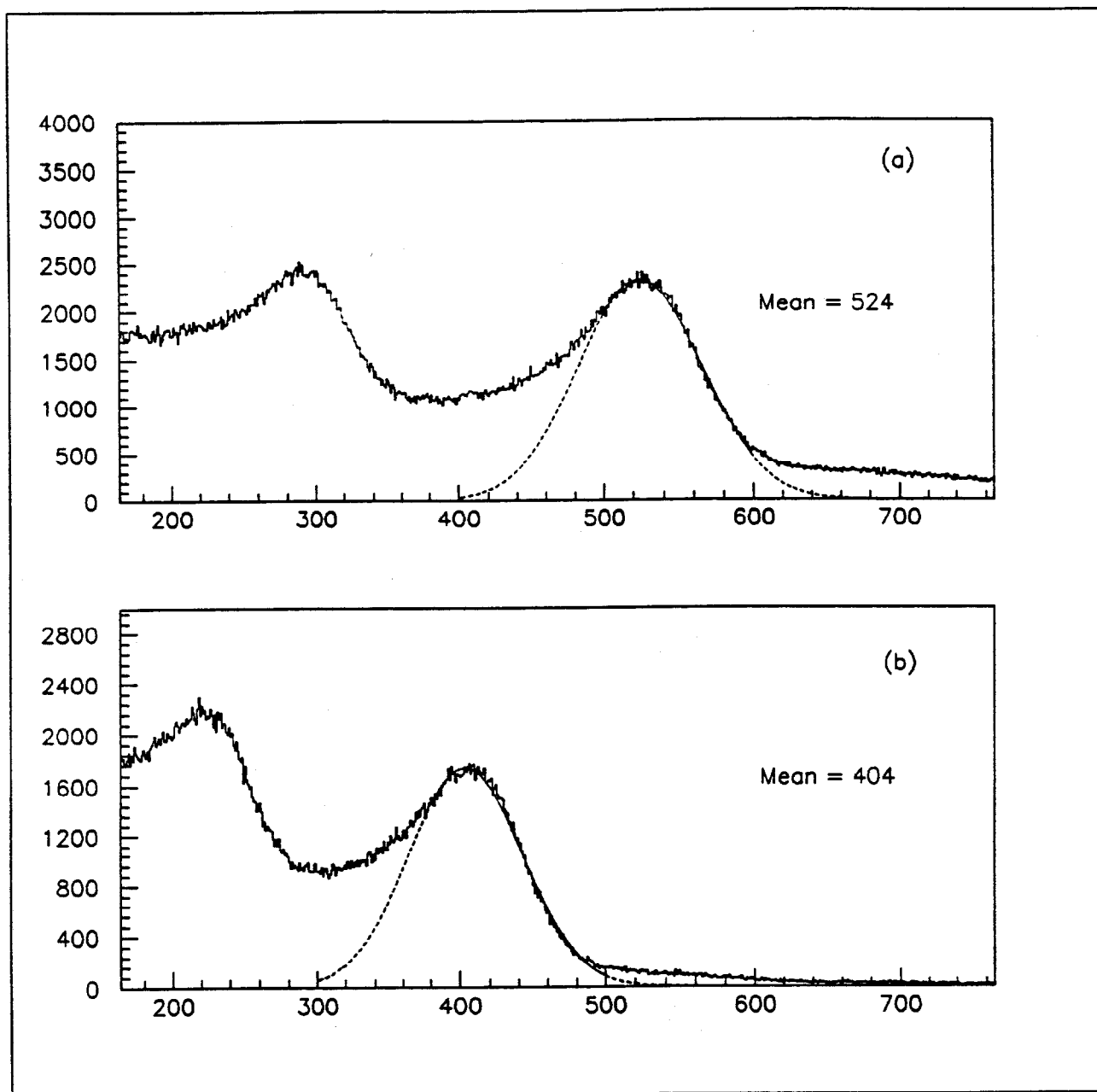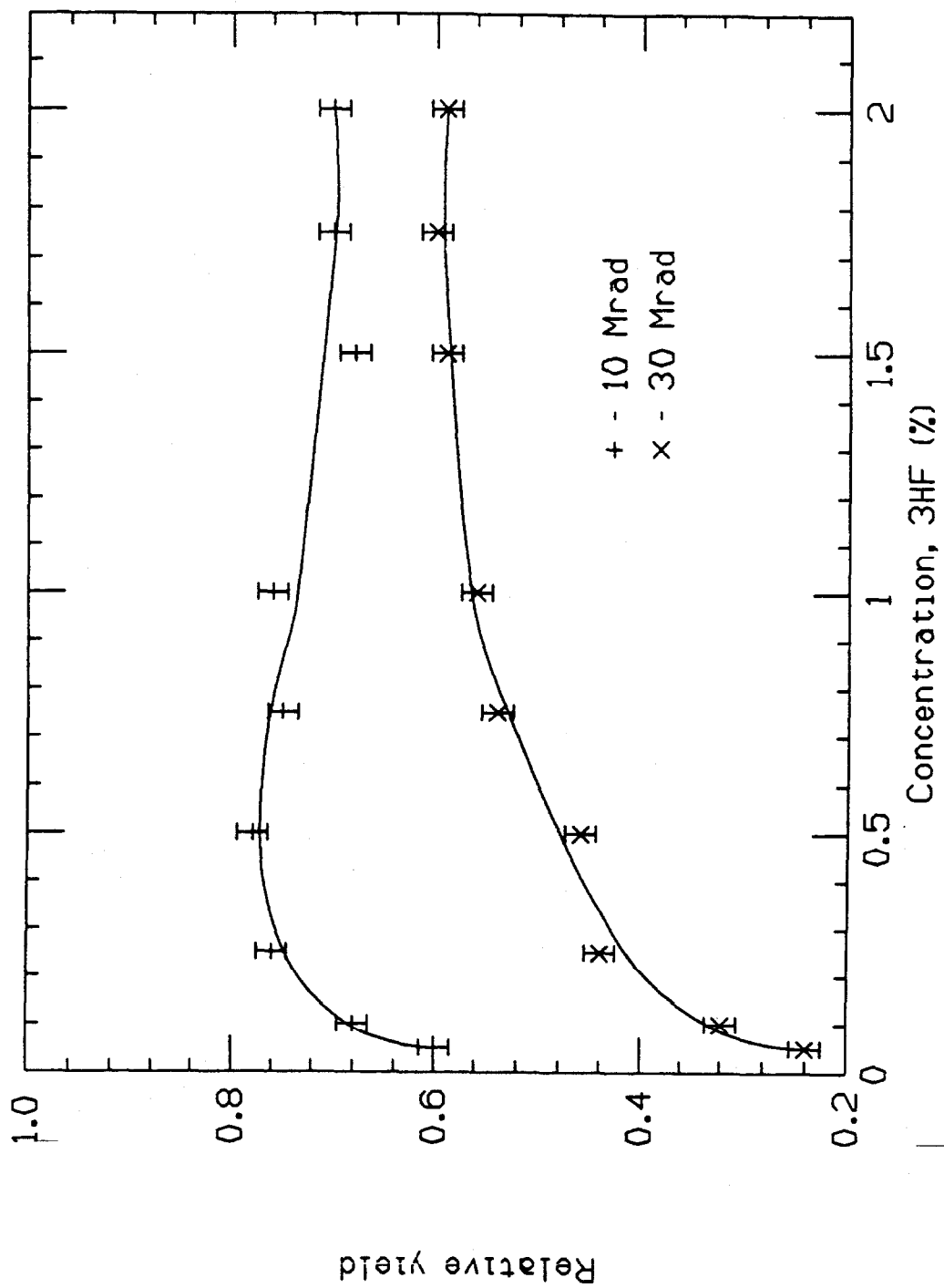
FIGURE 6

FIGURE 7
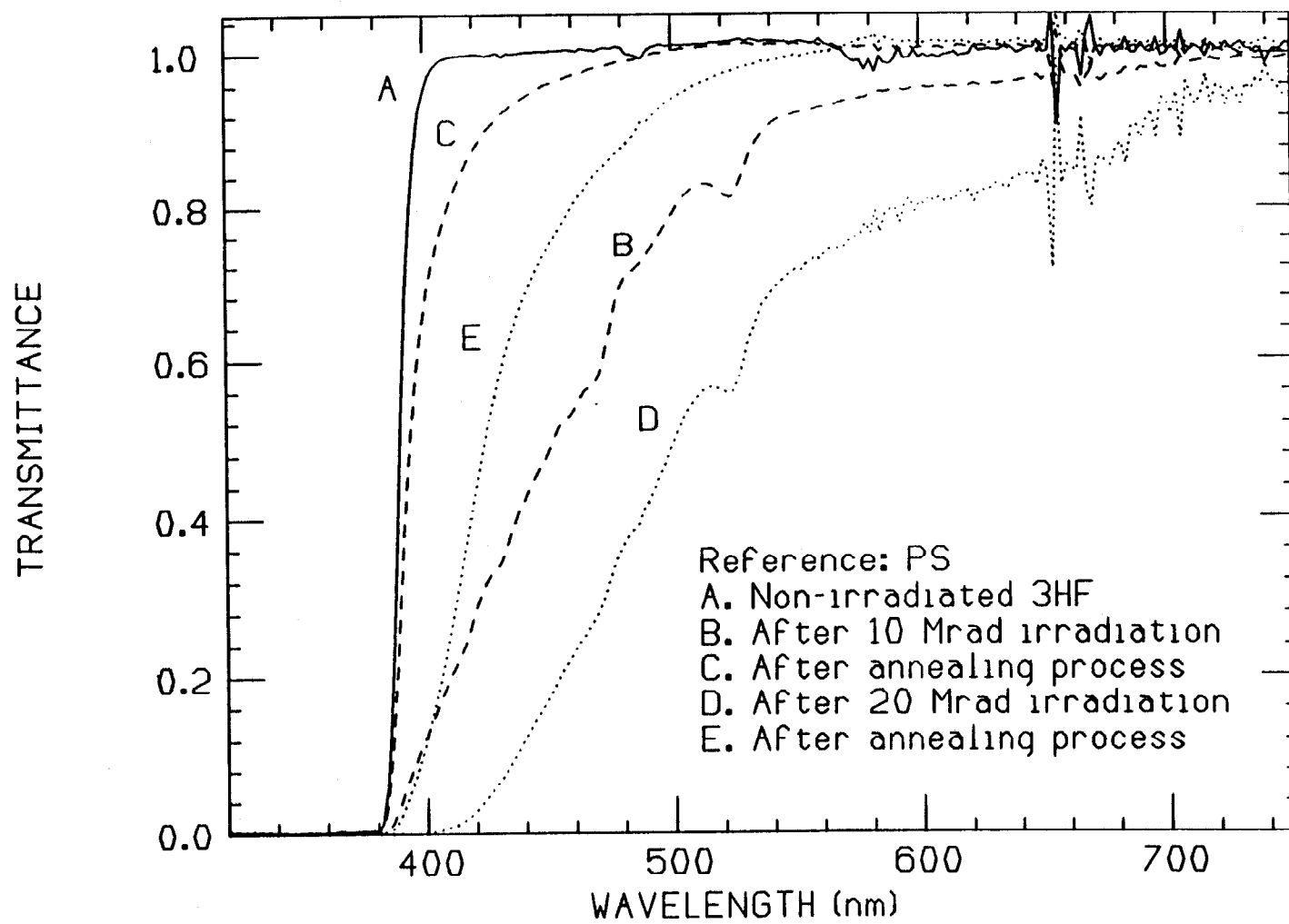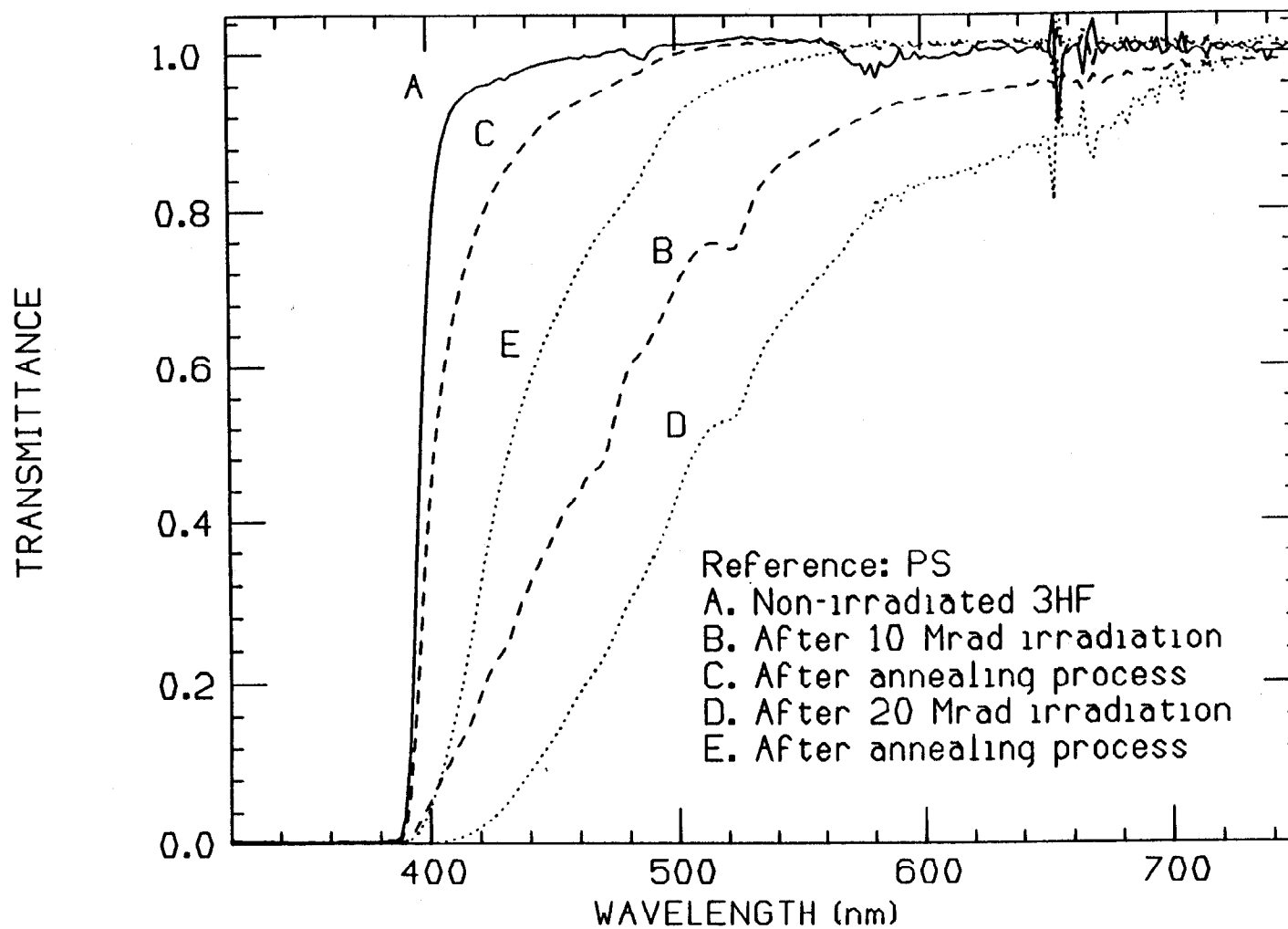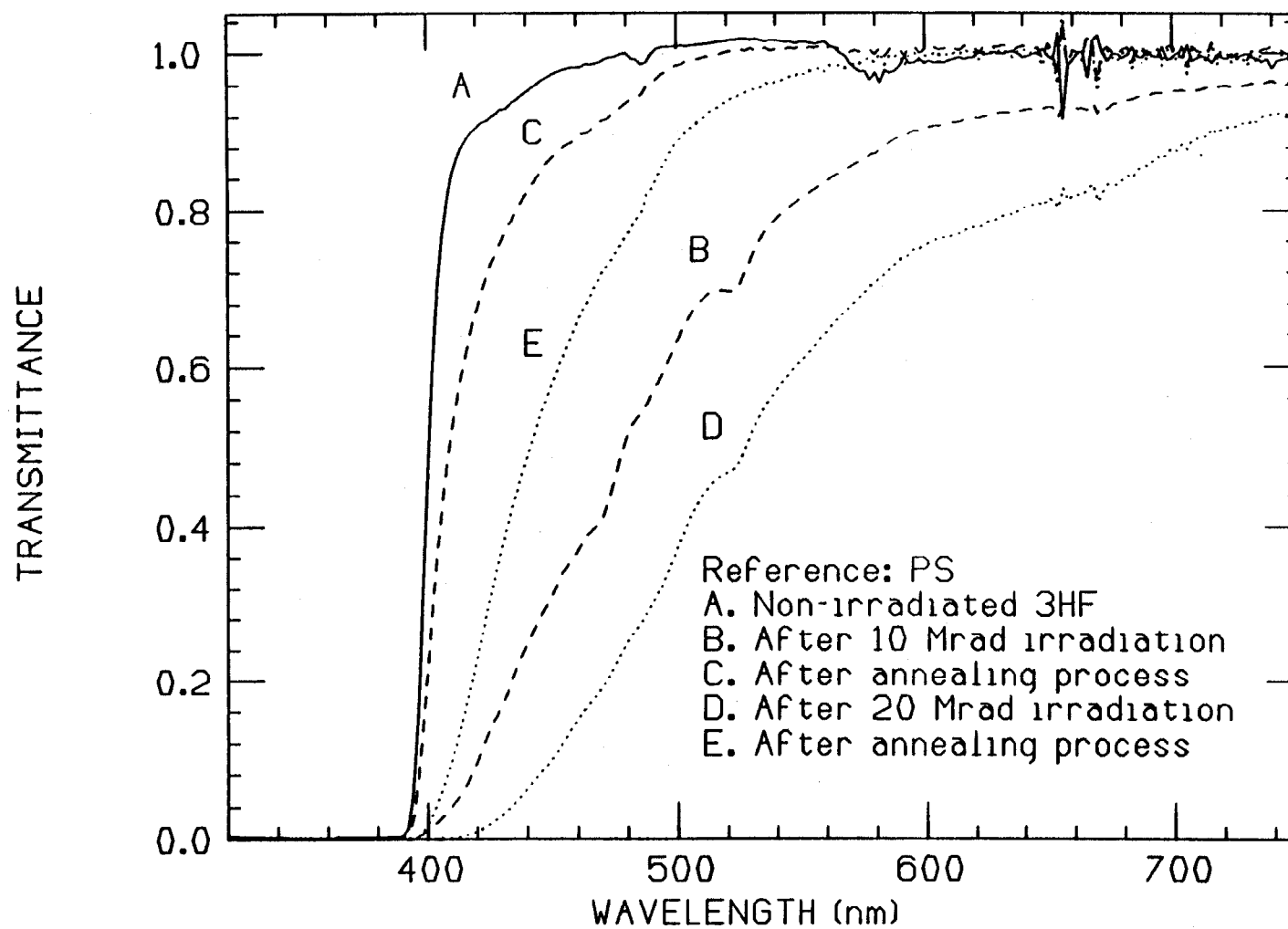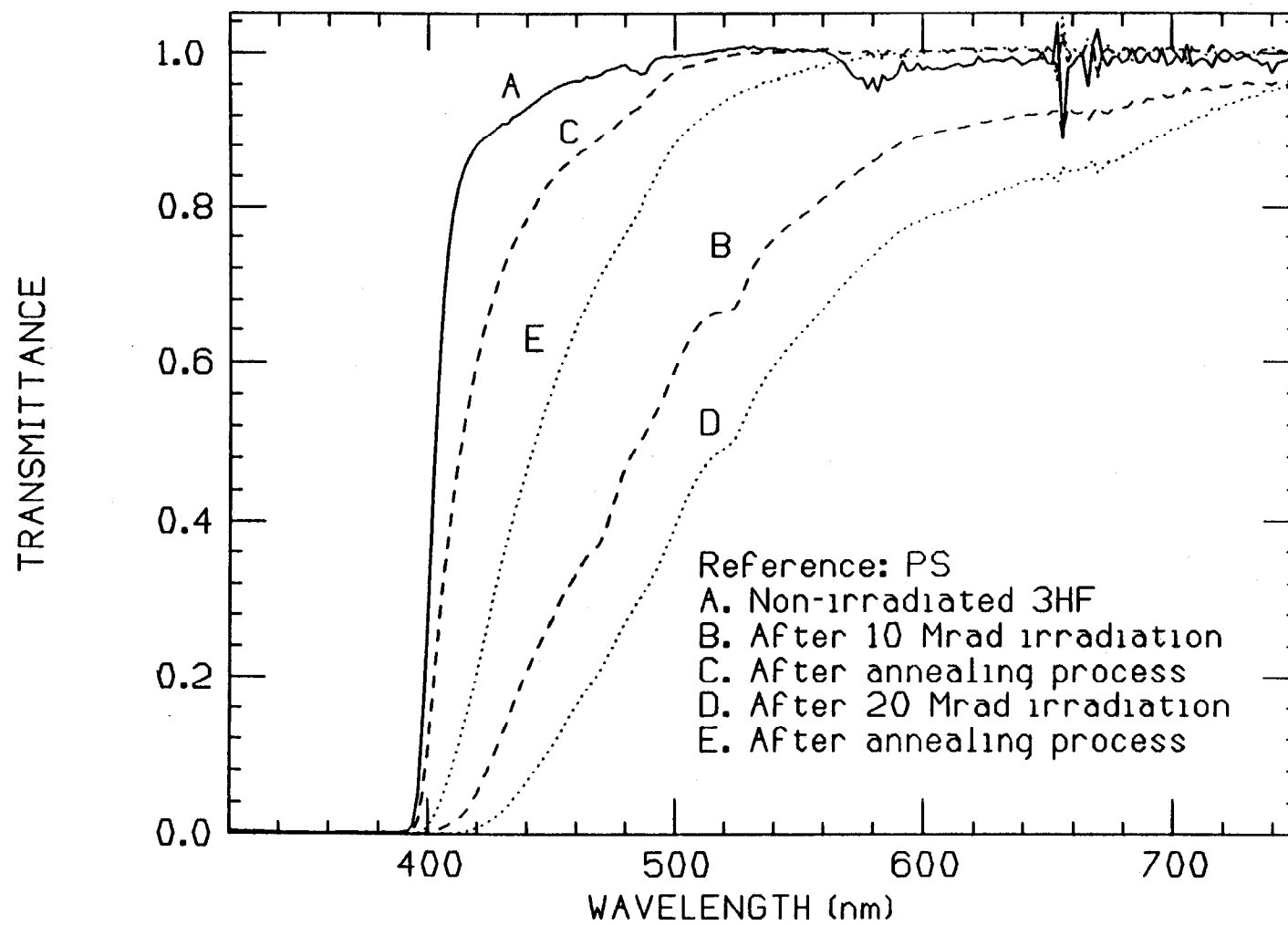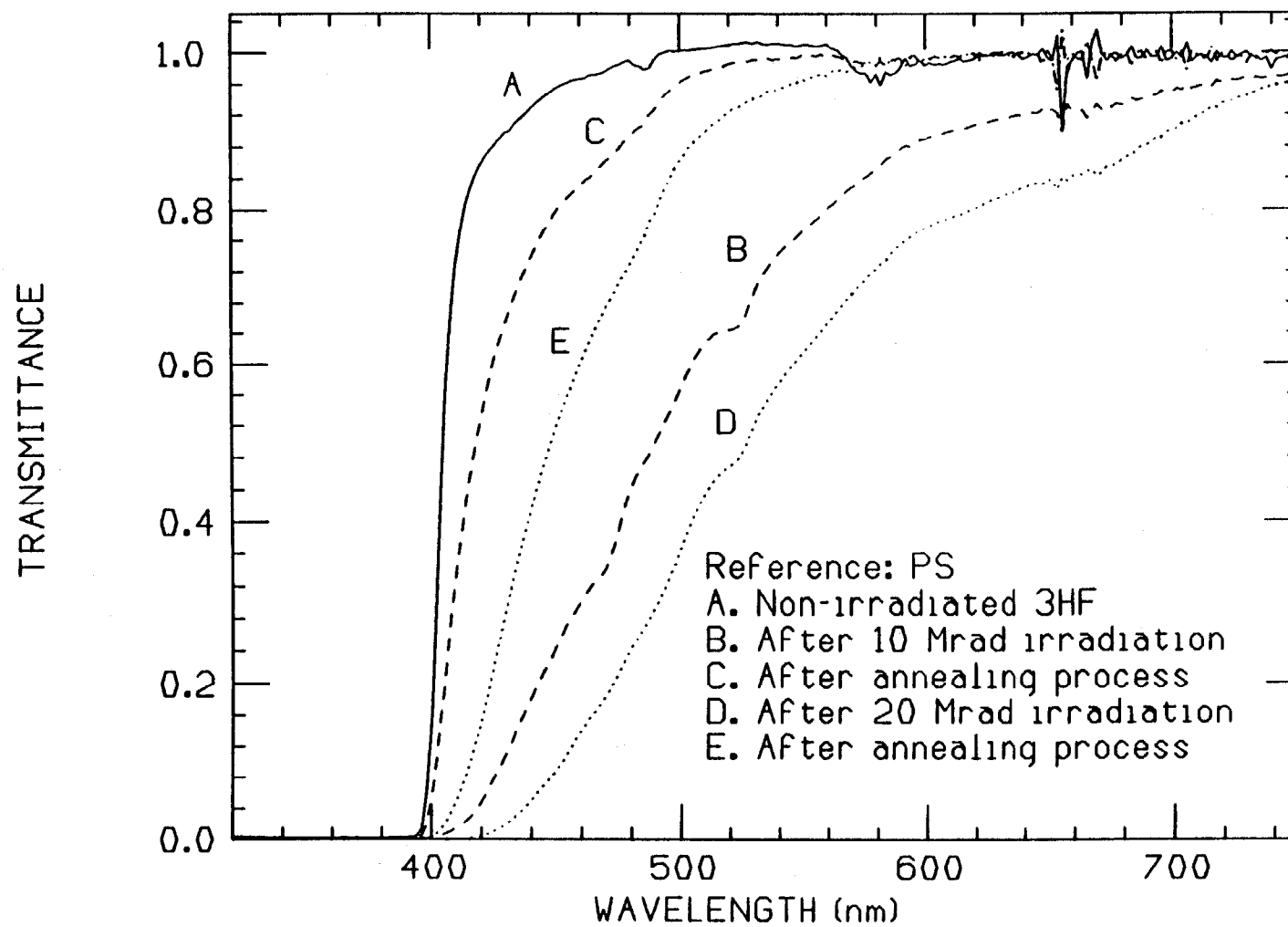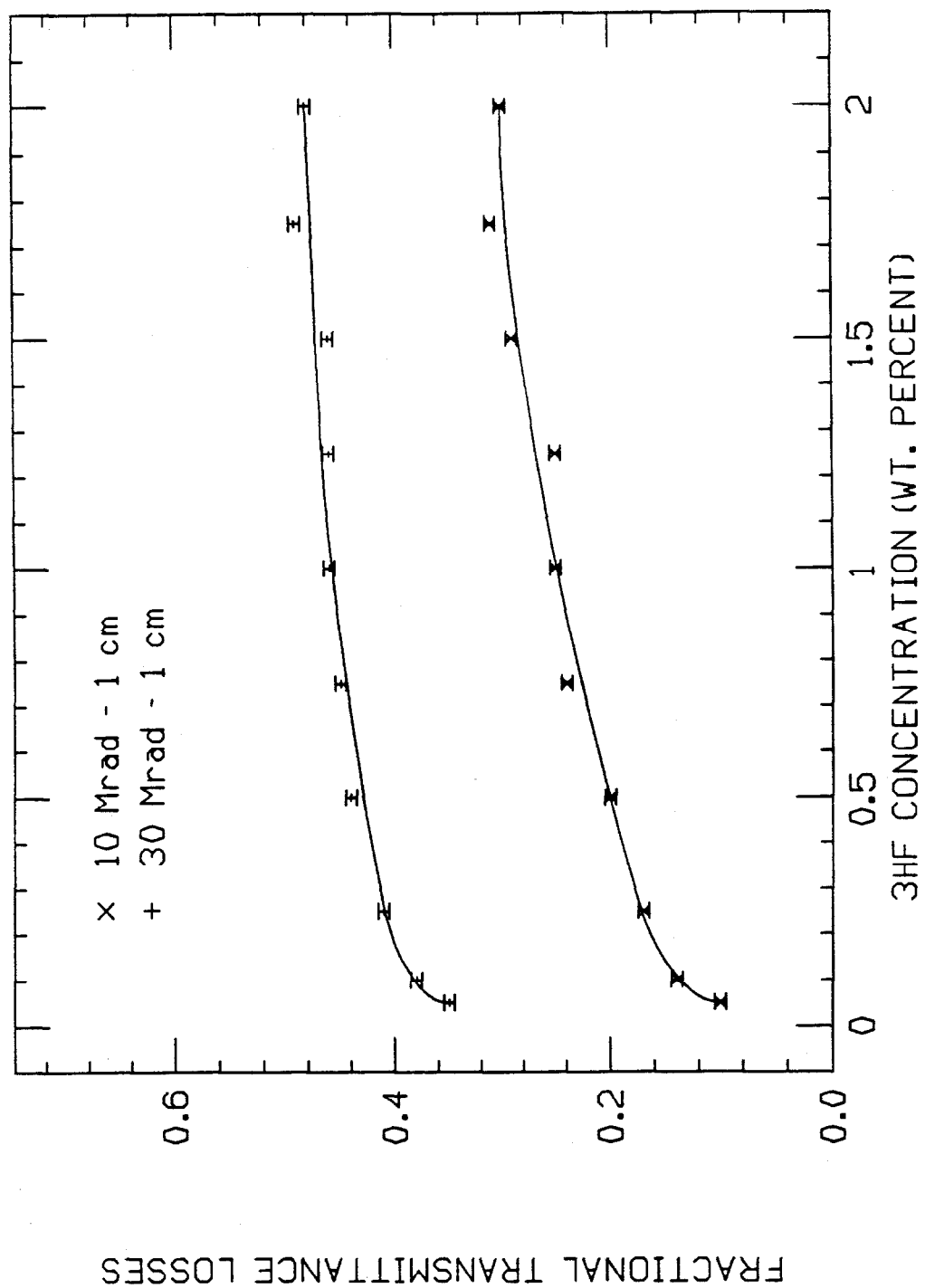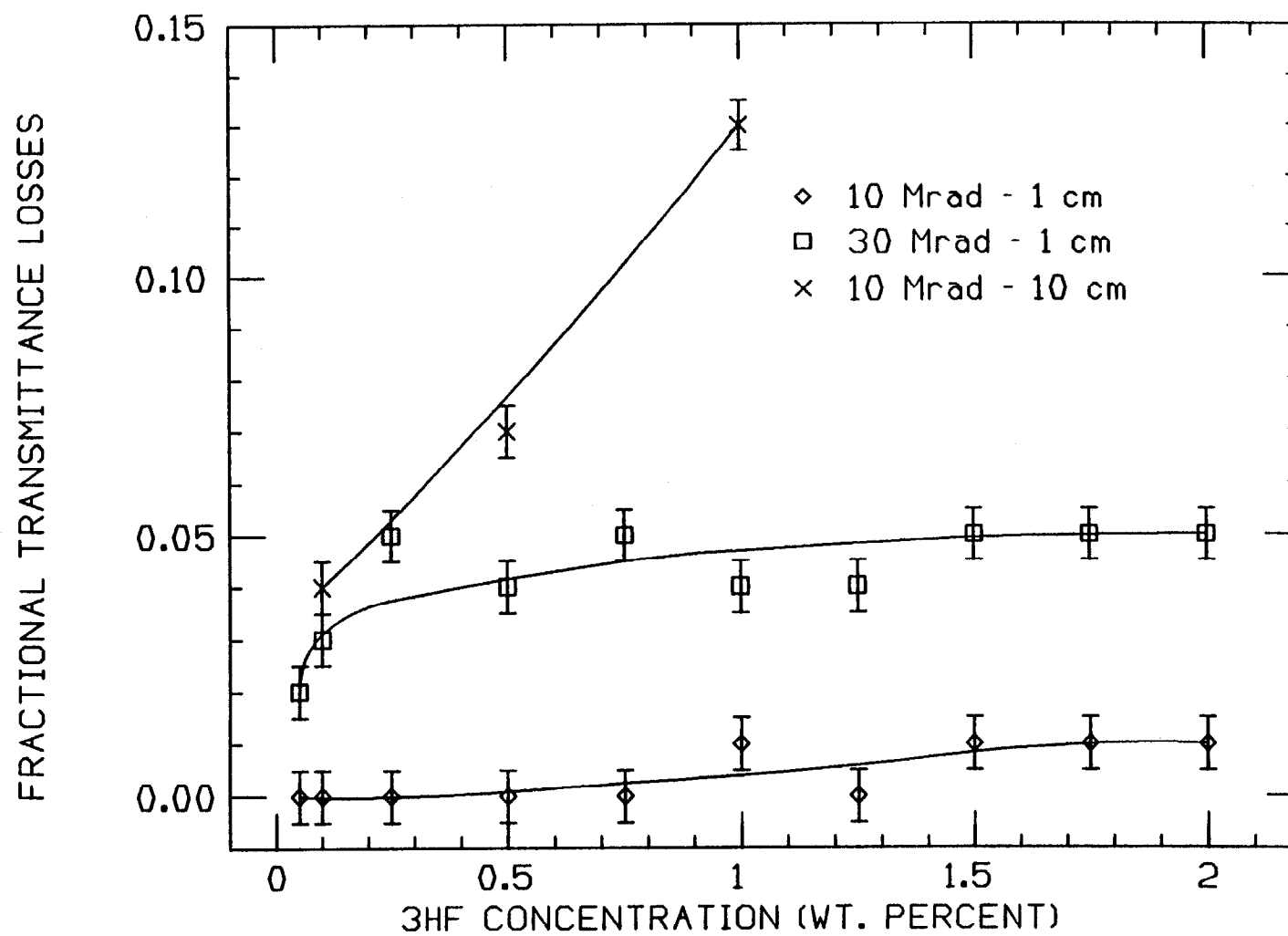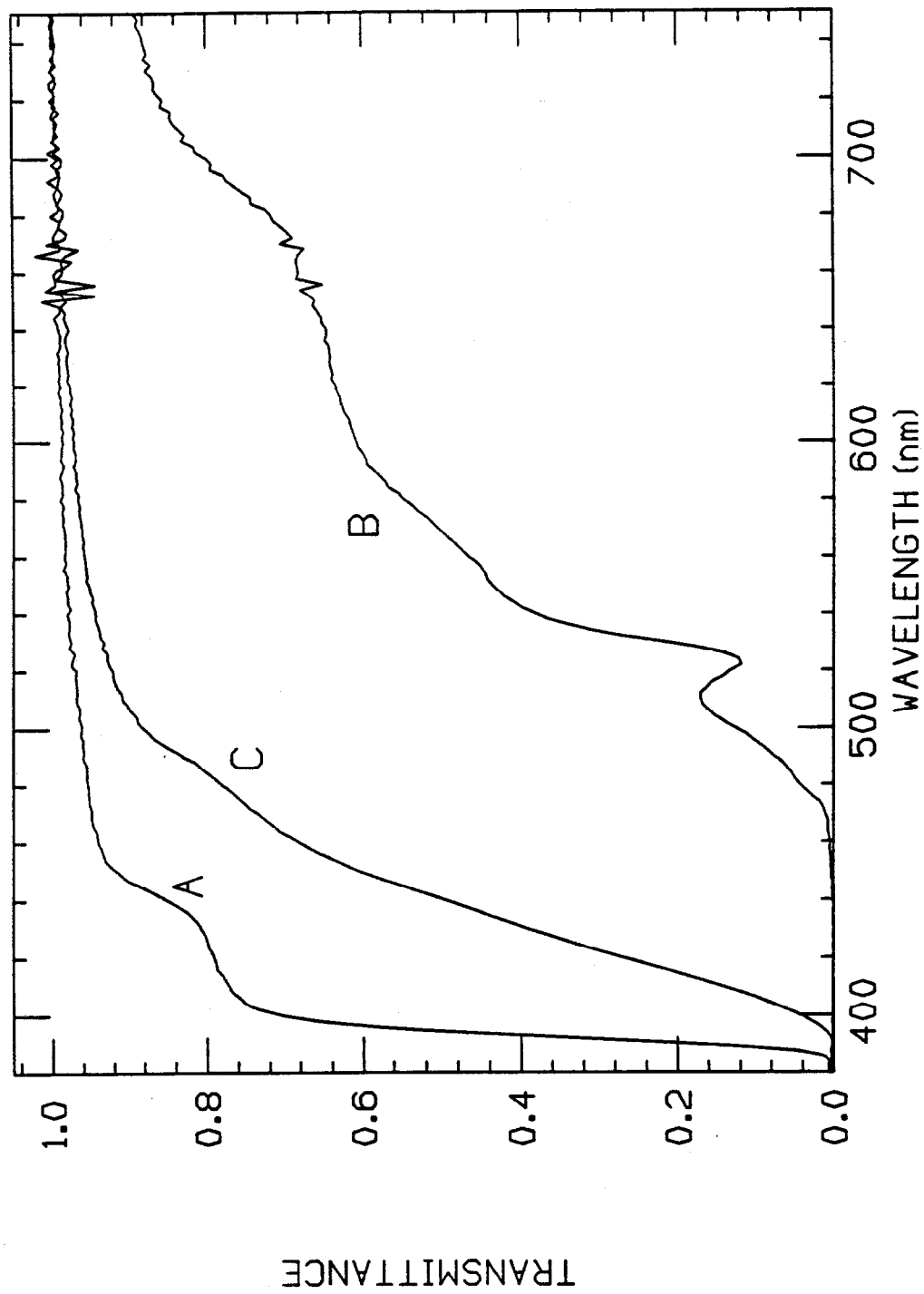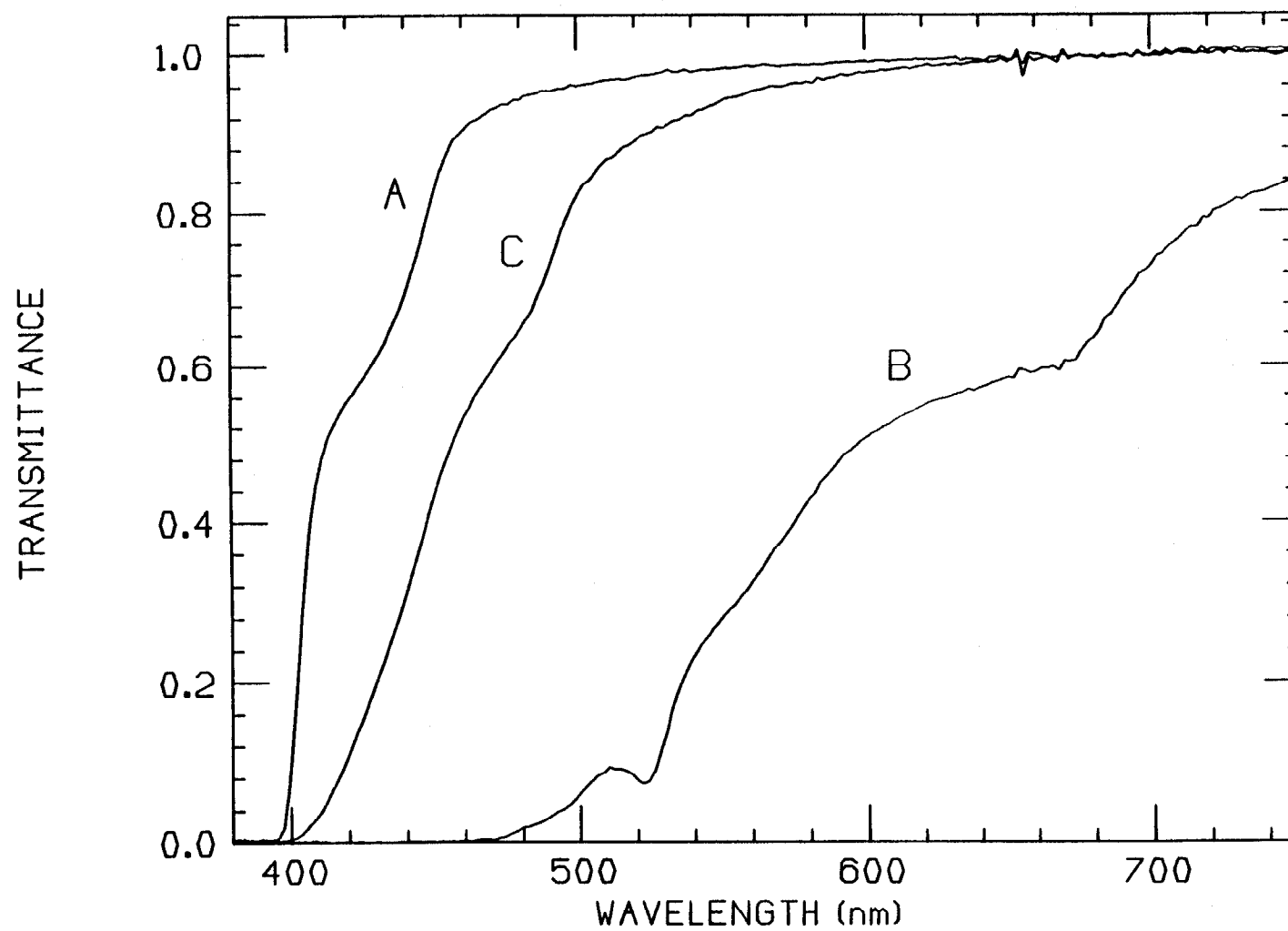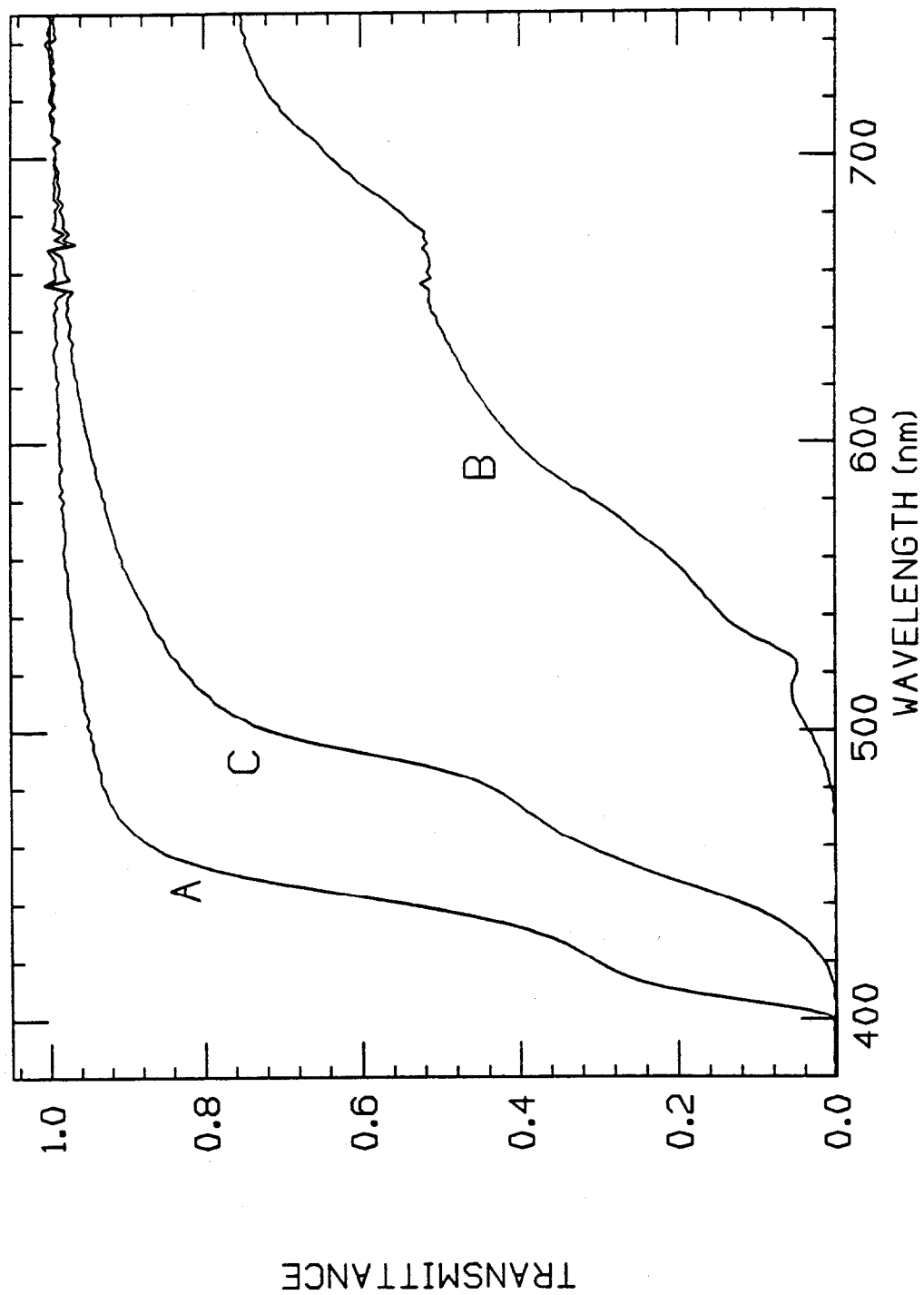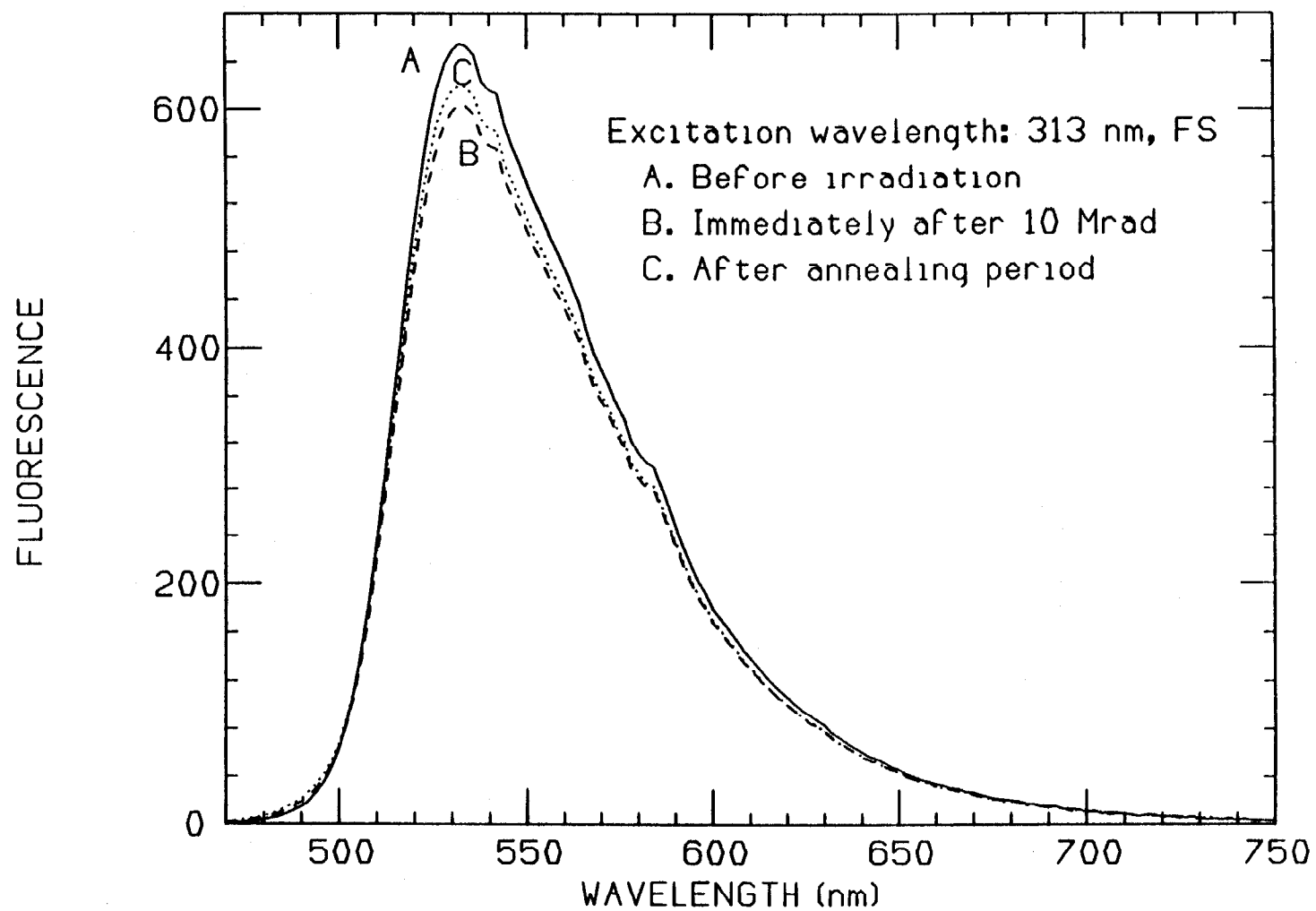
FIGURE 8

FIGURE 9

FIGURE 10

Reference: PS
A. Non-irradiated 3HF
B. After 10 Mrad irradiation
C. After annealing process
D. After 20 Mrad irradiation
E. After annealing process

FIGURE 11

Reference: PS
A. Non-irradiated 3HF
B. After 10 Mrad irradiation
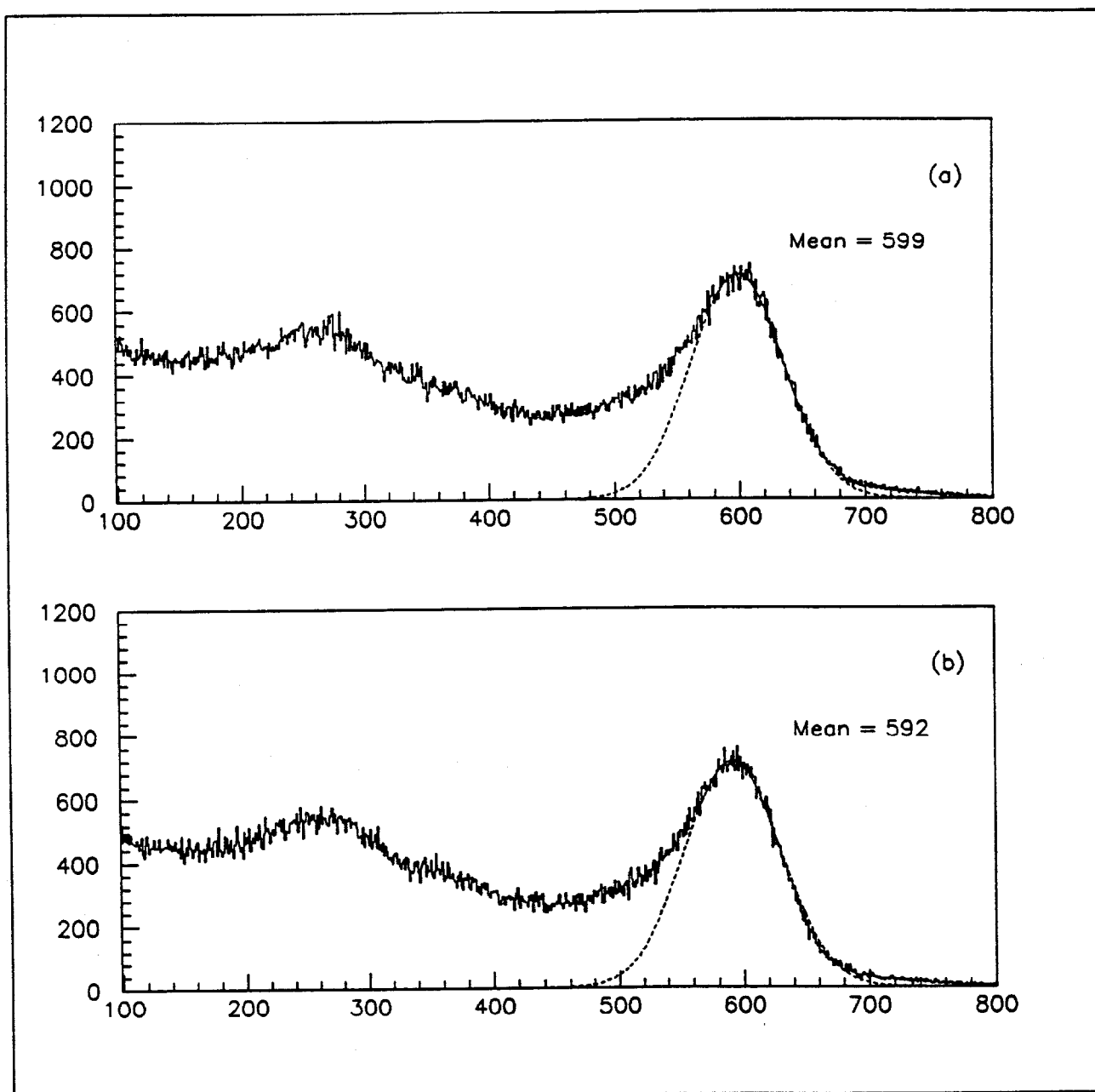C. After annealing process
D. After 20 Mrad irradiation
E. After annealing process

FIGURE 12

FIGURE 13

FIGURE 14

FIGURE 15

FIGURE 16

TRANSMITTANCE

WAVELENGTH (nm)

FIGURE 17

FIGURE 18

FIGURE 19

1% 3HF IN POLYSTYRENE (0 Mrad)

POLYSTYRENE

3HF

Time (min.)

ABSORBANCE (mAU)

FIGURE 20

1% 3HF IN POLYSTYRENE (30 Mrad)

POLYSTYRENE

3HF

ABSORBANCE (mAU)

Time (min.)

FIGURE 21